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(54) LUBRICIOUS HYDROPHILIC COATING, RESISTANT TO WET ABRASION

GLEITFÄHIGE HYDROPHILE BESCHICHTUNG, BESTÄNDIG GEGEN NASSABREIBUNG

REVETEMENT LUBRIFIANT HYDROPHILE RESISTANT A L'ABRASION PAR VOIE HUMIDE

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Description

This invention relates to hydrophilic, lubricant coatings that make biomedical devices slippery when wet. The method and coating of the invention may be employed to reduce the coefficient of friction of catheters, condoms, contact lenses, peristaltic pump chambers, arteriovenous shunts, gastroenteric feed tubes and endotracheal tubes, or other implants of metal or polymer substrate.

Known lubricious coatings that may be applied to biomedical devices include coatings of polyvinylpyrrolidone (PVP), polyurethane, acrylic polyester, vinyl resin, fluorocarbons, silicone, rubber, or combinations of these substances.' For example, Micklus et al., U.S. 4,100,309 and U.S. 4,119,094 relate to a hydrophilic coating of PVP polyurethane interpolymer formed with polyisocyanate. Ratner et al., U.S. 3,939,049, relates to a method of grafting hydrogels to polymeric substrates using radiation. Hudgin et al., U.S. 3,975,350, relates to hydrophilic polyurethane polymers. Stoy et al., U.S. 3,987,497, relates to a tendon prothesis with hydrogel coating.

These known hydrogel coatings have disadvantages:

They may have an insufficiently low coefficient of friction, they may lack permanence (such as silicone or fluorocarbons), they may be slippery when dry as well as wet, making handling difficult, or (such as the Micklus *et al* coatings) they may require the use of hazardous solvents to prepare them and contain unstable, reactive materials, so that separate and new solutions must be prepared daily or more frequently.

Furthermore, in the PVP-polyurethane coatings, little control can be exerted over the degree of lubricity and resistance to wet abrasion of the coatings, and such coatings are often unstable.

In order to solve these problems a hydrophilic lubricant coating was needed which, when wetted, has sufficient lubricity to be useful for biomedical devices such as implants, which adhere to a wide variety of substrates and resist wet abrasion, and which can be prepared from chemically stable and biocompatible solvents.

WO89/07521 relates to coated polymer surfaces wherein the coating comprises a polyvinylpyrollidone that is reacted with a silane compound to provide cross-linking. A further component may be a "tie coat" such as poly (methyl vinyl ether/maleic anhydride).

SUMMARY OF THE INVENTION

One embodiment of the present invention relates to a hydrophillic coating which comprises a hydrophillic polymer and a stabilizing polymer in a layer bonded to the surface of the device. The hydrophillic polymer is preferably PVP or PVP vinyl acetate. The stabilizing polymer is a water-insoluble polymer that does not significantly react with the hydrophilic polymer in solution, and is preferably cellulose ester, a copolymer of polymethyl vinyl ether and maleic anhydride, or nylon. The cellulose esters are most preferred. They include ethyl cellulose, hydroxyethyl cellulose, cellulose nitrate, cellulose acetate, cellulose acetate butyrate, and cellulose acetate proprionate.

In one embodiment, the coating has an inner layer where the stabilizing polymer is concentrated and an outer layer where the hydrophilic polymer is concentrated. In another embodiment, the hydrophilic polymer and stabilizing polymer are contained in a single application and comprise a single layer of coating.

The coating may also contain an adherent polymer such as polyurethane, polyester, styrene polybutadiene, acrylic resin, polyvinylidene chloride, polycarbonate, and polyvinyl chloride, preferably in the inner layer to promote adhesion to the surface of the device.

A most preferred outer layer composition uses PVP of high molecular weight (e.g. 120,000-360,000).

The inventive coating may be applied to a polymer surface such as polyurethane, polyvinyl chloride, polyacrylate, polycarbonate, polystyrene, polyester resin, polybutadiene- styrene copolymers, nylon, polypropylene, polybutylene, teflon, silicon, and polyvinyl acetal. The coating of the invention can also be applied to glass or metals such as stainless steel. The coating components can be selected to produce a coating with desired properties on these surfaces.

The method of preparing the coatings of the invention employs stable, non-toxic solutions which may be stored and handled with minimal precautions. The method of applying the coating of the invention comprises preparing a first organic solution of from about 0.01% to about 30% weight to volume of stabilizing polymer, preferably from about 0.2% to about 10%, applying the solution to a substrate surface, and evaporating the solvent, preferably at elevated temperature, then preparing a second solution Of from about 00.01% to about 30% Weight to volume hydrophilic polymer, preferably from about 0.5% to about 20%, applying it to the treated surface substrate and evaporating the solvents at room or elevated temperature.

The stabilizing polymer solution may also contain from about 0.01% to about 10% of hydrophilic polymer, preferably from about 0.1% to about 5%. The hydrophilic polymer solution may also contain from about 0.01% to about 20% of stabilizing polymer, preferably from about 0.1% to about 10%. Alternatively, the stabilizing polymer and hydrophilic polymer can be prepared in a single solution and applied in a single step.

The surface of the device may be pre-treated to promote adhesion of the coating. The solutions may also contain from about 0.1% to about 15% of an adherent polymer, preferably from about 1.0% to about 8.0% weight to volume to

promote the bond between substrate and coating.

A plasticizing agent may be included with the stabilizing polymers, in a concentration of from about 0.01% to about 10%, preferably from about 0.1% to about 5.0%, weight to volume. The plasticizing agent may be camphor, castor oil, dioctyl phthalate, acetyl tributyl citrate, dibutyl sebacate, sebacic acid, alkyl resin, dibutylphthalate, polyvinylbutyral or other commonly known plasticizers, singly or in combination. The plasticizing agent is preferably included in the solution of stabilizing polymer. The inventive coating may include a plasticizer to enhance the flexibility of the coating, which may be preferable when the object to be coated is likely to bend during use. Also, the inclusion of a plasticizer is preferred when the stabilizing polymer is nitrocellulose, because the plasticizer reduces the tendency of nitrocellulose to oxidize rapidly or even combust when it is dried in a pure form.

Solvents for the stabilizing and adherent polymer include organic solvents such as ketones, esters, toluene, lactones, dimethylformamide, halogenated solvents, tetrahydrofuran, dioxane, amines, glycol butyl ether, alkyl acetates, acetonitrile, and other commonly known organic solvents. The less toxic solvents are preferred. The inclusion of small amounts of hydroxyl groups such as alcohols and moisture in the solvent does not have a significant detrimental effect on the coating and method of the invention.

Solvents for the hydrophilic polymer include most of the above as well as alcohols, acetic acid, and like solvents. A solvent system may be selected that is capable of dissolving all the constituents of the coating in a uniform solution, can act as a co-solvent in the layer, and is non-toxic.

If desirable, a solvent may be selected that interacts with the particular substrate surface to promote adhesion.

In another embodiment of the present invention, the article to which the coating is to be applied has a polymer surface and an "active" solvent is used which obviates the need for the inner layer or base coat by permitting a lubricious hydrophilic layer (or top coat) to be applied directly onto the polymer surface of the article. In this embodiment, the term "active solvent" is defined as a cosolvent for both the polymer or polymer mixture comprising the polymer surface or at least one or more of the polymers in cases of mixed polymer substrates and for the coating polymer(s).

The solutions may be applied by dipping the object to be coated into a vessel containing the solution, or the solutions may be poured, pumped, brushed or sprayed onto the object.

DETAILED DESCRIPTION OF THE INVENTION

The hydrophilic coatings of this invention are highly lubricious when wetted with an aqueous solution such as body fluid, or a lower alcohol such as ethanol or methanol, yet they are substantially less slippery when dry. Thus, an implant coated according to the invention remains non-slippery for ease of handling and preparation, but becomes lubricious when implanted, so as to protect the patient. The lubricity of the coating can be adjusted within a desirable range.

A coating according to the invention may be applied to the surface of a biomedical or other device with sufficient thickness and permanence to retain the coating's desirable qualities throughout the useful life of the coated device. The coatings of the invention are non-reactive with living tissue and are non-thrombogenic in blood.

The coating of the invention has beneficial characteristics for use on the surfaces of devices such as biomedical implants. The coating is hydrophilic, absorbing water and swelling in an agueous environment to become a hydrogel. The coating has lubricant properties, and is significantly more slippery when wet than when dry. The coating is thin, on the order of magnitude of one thousandth of an inch. The coating is coherent and resistant to removal by wet abrasion, and it is adherent to a wide variety of substrates. The coating employs biocompatible substances that are neither toxic nor irritant. The functional characteristics of the coating may be varied as appropriate for many different applications.

The method of the invention is beneficial because the components can be varied to control lubricity, swelling, flexibility, and resistance to removal by wet abrasion. These characteristics of the coating can thus be adjusted for various substrates and applications. The method is also beneficial because the solutions of the invention have good shelf stability and remain substantially free of precipitate for periods in the range of months or years, so that various mixtures of the solutions for coatings may be prepared at one time and used to :oat substrates later. Alternatively, the hydrophilic and stabilizing polymers, and if desired, a plasticizing agent and an adherent polymer, may even be prepared in a single solution. Furthermore, since the invention does not require the use of chlorinated solvents or other acute toxics, fewer precautions are necessary to protect workers from health hazards.

Without intending to limit the invention to its mode of operation, apparently the stabilizing polymers of the invention, particularly modified cellulose polymers, are able to make hydrophilic polymers, such as PVP and PVP-vinyl acetate copolymers, stable and insoluble in water and lower alcohols. The resulting combination, when applied to a substrate, produces a coating that is a stable layer or layers that are bonded to a substrate surface, is not slippery when dry but is desirably lubricious when wet, and is resistant to removal by conditions of wet abrasion. The coating layer bonds to an impervious surface such as stainless steel or glass. It also bonds to polymer surfaces where the surface interacts with the components of the coating.

It is possible to control the degree of stability, wet lubricity, insolubility, flexibility, and adhesion of the coating by varying the weight to volume percentages of the components in the coating solutions. Substantially all of the polymers and

plasticisers deposited from solutions onto the surface of the object being coated remain in the layer of the coating after the solvents are evaporated. Also, the duration and temperature of the evaporating step may be selected to achieve stability of the coating layer and to achieve a bond between the surface being coated and the coating layer.

Preferably, the outer layer solution contains some amount of an "active" solvent, i.e., a cosolvent, for the outer layer ingredients as well as the inner layer ingredients. As such, the active solvent causes the outer layer solution to penetrate into the inner layer, and is believed to bring about a mixing at the molecular level of the components of both layers.

It is believed that such molecular mixing may lead to chemical reactions such as cross-linking between the components, or may only comprise physical mixing without chemical reaction(s). In any event, in one preferred embodiment, there is a high degree of cross-linking or intermolecular mingling between the hydrophilic polymer and the stabilizing polymer at the interface between the inner and outer layers of the coating relative to the outer surface of the outer layer. Thus, an interpolymer between the two layers may be created as a result of cross-linking or intermolecular mingling between the polymers contained in the separate layers. The slight degree or lack of cross-linking at the outer surface of the coating aids in providing the lubricity of the coating of the present invention.

In practice, the activity of the solvent mixture is adjusted so that the degree of penetration of the outer layer into the inner layer is in a useful range. For example, if the outer layer solvent mixture is too active toward the inner layer, then too much penetration into the inner layer occurs, and the outer layer will not be sufficiently lubricious when wet. Conversely, if the outer layer solvent is too inactive toward the inner layer, then too little penetration of outer layer into the inner layer occurs, and the coating is too easily removed from the inner layer by wet abrasion.

In another embodiment of the present invention, where the lubricious hydrophilic layer is applied directly onto a polymer surface as a top coat, and an active solvent is used which is a cosolvent for both the plastic substrate polymer or polymer mixture or at least one or more of the polymers in cases of mixed polymer substrates, and for the coating polymer(s) in the hydrophilic layer.

After drying, which is typically done at temperatures between 50°C and 100°C, but may be done at higher or lower temperatures, the top coat polymer(s) layer is left partially embedded in the polymer surface. As in the case of the two-layer system, the solvent used during the coating application can be too active such that the top coat penetrates into the polymer surface to such a degree that the coated layer behaves as though it has been highly cross-linked. This causes the top coat to not become sufficiently swollen and lubricious when wet by aqueous fluids. Solvent mixtures can also be too inactive, so that the coating is not resistant enough to abrasion when wet and is too easily removed.

As in the two-layer systems, other polymers or cross-linking agents may be incorporated with the hydrophilic polymer(s) in the lubricious layer to enhance the adhesion of the layer to the polymer surface, making the lubricious layer more resistant to wet abrasion.

The active solvents which are useful in the present invention may be individual solvents or solvent mixtures containing two or more solvents. In the case of solvent mixtures, one or more of the solvents in the mixture may be active while other solvent(s) in the mixture may be inactive. In any event, the solvent or solvent mixture dissolves or at least disperses the top coat polymer(s). In cases where the top coat polymer is dispersed but not dissolved, a point is reached where the top coat polymer(s) go into solution before all of the solvent has left the coating. During the phase of drying where the top coat polymer(s) is in solution, the solvent has also penetrated the substrate polymer(s) of the polymer surface. Thus, intermolecular mingling may take place between the substrate polymer(s) and the top coat polymer(s).

Examples of active solvents useful in the present invention include butyrolactone, alcohols, dimethyl acetamide, and n-methyl-2-pyrrolidone. These solvents and others cause different degrees of swelling of the plastic substrate or inner layer, as the case may be.

The hydrophilic polymers of the coatings are generally PVP of higher molecular weight, 120,000-360,000. PVP of lower molecular weight, as low as 15,000, can be used in the underlayer or base coating next to the substrate without deterioration of performance. Some or all of the PVP can be replaced with PVP-vinylacetate copolymer in the one-coat embodiment, or in either layer of the two-coat embodiment.

It has been found that the most preferred stabilizing polymer is a water insoluble cellulose polymer. Alternatives to modified cellulose polymers, such as polymethylvinylether maleic anhydride and nylon may be used instead of or in addition to the modified cellulose polymers, but these are more difficult to work with, and tend to produce coatings with less long-term wet abrasion resistance than coatings prepared without them. When the stabilizing polymer is nitrocellulose, it is preferable to include a plasticizing agent.

When tested by subjective methods the coatings of the invention, when wet, are more slippery than wet, greased glass, and, when dry, are no more slippery than dry glass. The coatings of the invention are resistant to removal by wet abrasion as determined by running water over the coatings and rubbing between tightly gripped fingers while wet. The inventive coatings have high adherence when dry, as determined by attaching adhesive tape, pulling the tape off with a vigorous action, and then wetting the coated substrate to determine whether the taped portion retained the lubricant coating. The inventive coatings remain adherent and coherent for extended periods when stored in water, and neither peel off, dissolve, nor dissociate.

The coating systems described herein will produce hydrophilic lubricant coatings, resistant to wet abrasion on surfaces such as polyethylene, polypropylene, silicon, glass, stainless steel, and other substrates generally considered as presenting adherence problems. It may be necessary to treat such surfaces with gas plasma or other ionizing treatment to promote adhesion to the substrates. The following examples show how the invention can be used.

EXAMPLE 1:

Polyurethane tubing was dip coated in a stabilizing polymer solution of

5.4 gm low viscosity 1/2 second nitrocellulose
2.0 gm dibutylphthalate
1.5 gm camphor
1.9 gm polyvinylbutyral in a solvent mixture of
36.0 ml toluene
13.1 ml butylacetate
5.9 ml isopropanol
25.4 ml ethylacetate
18.1 ml ethanol
1.5 ml acetone.

The coated tube was dried for 5 minutes at 65°C. It was then dip coated with a hydrophilic polymer solution containing

6.6 gm polyvinylpyrrolidone
63.8 ml denatured ethanol
23.6 ml ethyl acetate
12.6 ml dimethylformamide

and dried 5 minutes at 65°C. A hydrophilic coating resulted which was slippery when wet.

EXAMPLE 2:

Styrenebutadiene tubing was dip coated in a stabilizing polymer solution containing 1.9 gm 1/2 second nitrocellulose together with a hydrophilic polymer, 1.5 gm polyvinylpyrrolidone, in

60 ml ethylacetate
34.4 ml denatured ethanol
4.6 ml acetic acid
1 ml isopropanol

and dried 5 minutes at 80°C. The sample was then dip coated in a hydrophilic polymer solution containing 7.5 gm polyvinylpyrrolidone together with a stabilizing polymer, 0.3 gm nitrocellulose, in

73 ml denatured ethanol
26.8 ml ethylacetate
0.2 ml isopropanol

and dried 5 minutes at 80°C. A hydrophilic coating resulted that was lubricious when wet.

EXAMPLE 3:

Polyurethane tubing was dip coated with a stabilizing and hydrophilic polymer solution containing 5.9 gm 1/2 sec. cellulose acetate butyrate and 5.9 gm polyvinylpyrrolidone in 33 ml ethyl acetate and 67 ml chloroform and dried 5 minutes at 80°C. This was then dip coated in a hydrophilic polymer solution containing 5 gm polyvinylpyrrolidone in 95 ml denatured ethanol and dried 5 minutes at 80°C. A hydrophilic coating resulted that was lubricious when wet.

EXAMPLE 4:

Samples of polyurethane tubing were coated with a stabilizing and adherent polymer solution containing

1.9 gm nitrocellulose
1.1 gm polyester resin
1.0 gm monobutylester of polymethylvinylether/maleic anhydride copolymer
0.8 ml isopropanol
57.8 ml ethylacetate
33.4 ml denatured ethanol
8 ml dimethylformamide.

The sample was dried five minutes at 80°C. The samples were then dip coated in a hydrophilic polymer solution containing

6.6 gm polyvinylpyrrolidone
63.8 ml denatured ethanol
23.6 ml ethylacetate
12.6 ml dimethylformamide

The sample was dried five minutes at 80°C, to produce an adherent, lubricious, layered coating. A similar coating was also produced on polyvinylchloride tubing.

EXAMPLE 5:

This example shows how different "adhesive" resins can be added to promote adhesion to a substrate.

a. The following stabilizing polymer solution was dip coated on polyurethane tubing and dried 5 minutes at 80°C.

nitrocellulose	56 gm
camphor	15 gm
dibutylphthalate	20 gm
isopropanol	23 ml
toluene	225 ml
ethyl acetate	330 ml
butyl acetate	96 ml
acetone	7 ml

This was then dip coated with a hydrophilic polymer solution:

polyvinylpyrrolidone (PVP)	3 gm
denatured ethanol	27 ml
ethyl acetate	10 ml
dimethylformamide	12 ml

The coating separated from the tubing when immersed in water.
b. Example 5(a) was repeated with from 5.0 gm to 17 gm of polyurethane resin added to the nitrocellulose solution to produce samples that showed excellent adhesion when immersed in water.
c. Example 5(a) was repeated with from 5.0 gm to 17.0 gm polyester resin added to the nitrocellulose solution to produce samples that showed excellent adhesion when immersed in water.
d. Example 5(a) was repeated with from 5.0 gm to 17.0 gm of styrene butadiene resin added to the nitrocellulose solution to produce samples that showed excellent adhesion when immersed in water.

e. Example 5(a) was repeated with from 5.0 gm to 17.0 gm of urea formaldehyde resin added to the nitrocellulose solution to produce samples that showed excellent adhesion when immersed in water.

EXAMPLE 6

Polyurethane tubing was coated with the following stabilizing polymer solution and dried five (5) minutes at 65°C.

nitrocellulose	65 gm
dibutylphthalate	24 gm
camphor	18 gm
polyvinylbutyral	23 gm
acetone	28 ml
ethanol	306 ml
butyl acetate	257 ml
ethyl acetate	500 ml
toluene	550 ml
isopropanol	28 ml
dimethylformamide	200 ml

The sample was then overcoated with the following hydrophilic polymer solution and dried five (5) minutes at 65°C.

polyvinylpyrrolidone	1 gm
ethanol	9 ml
dimethylformamide	3 ml
water	0.5 ml

This sample had excellent adhesion when immersed in water.

EXAMPLE 7

An acrylic surface was coated with the following stabilizing polymer solution and dried five (5) minutes at 70°C.

cellulose acetate propionate	12.9 gm
dibutylphthalate	4.8 gm
camphor	3.6 gm
acetone	3.2 gm
ethyl acetate	55.7 gm
toluene	58.6 gm
butyl acetate	28.5 gm
isopropanol	5.6 gm

The sample was then coated with the following hydrophilic polymer solution and dried five (5) minutes at 70°C.

acetonitrile	5 ml
ethanol	4.5 ml
PVP (360,000 mw)	0.5 gm

The coating was not soluble in water and was very slippery.

EXAMPLE 8

An acrylic surface was coated with the following stabilizing polymer solution and dried five (5) minutes at 70°C.

cellulose acetate	12.9 gm
dibutylphthalate	4.8 gm
camphor	3.6 gm
methylethylketone	148.3 ml
dimethylformamide	20.0 ml

The sample was then coated with the following hydrophilic polymer solution and dried five minutes at 70°C.

PVP (360,000 mw)	0.5 gm
cellulose acetate	0.1 gm
acetone	6 ml
ethanol	4.5 ml
acetic acid	1.0 ml
methylethylketone	0.9 gm

The coating was insoluble in water and was very lubricious.

EXAMPLE 9

An acrylic surface was coated with the following stabilizing and adherent polymer solution and dried five minutes at 70°C.

cellulose acetate butyrate	6.5 gm
polyester resin	6.0 gm
dibutylphthalate	2.4 gm
camphor	1.8 gm
acetone	2.5 ml

(continued)

ethyl acetate	43.6 ml
toluene	43.6 ml
butylacetate	22.4 ml

The sample was then coated with the following hydrophilic polymer solution and dried five (5) minutes at 70°C.

acetonitrile	5 ml
ethanol	4.5 ml
PVP (360,000 mw)	0.5 gm

This coating was water insoluble and was lubricious when wet.

EXAMPLE 10

Nylon tubing was coated with stabilizing polymer with the following solution and dried ten (10) minutes at 75°C.

nylon resin	2 gm
trifluoroethanol	18 ml

The sample was then overcoated with hydrophilic polymer with the following solution and dried ten (10) minutes at 75°C.

PVP (360,000 mw)	1.0 gm
nylon resin	0.3 gm
ethanol	9.0 ml
dimethylformamide	3.0 ml
trifluoroethanol	2.7 ml

This coating was not water soluble.

EXAMPLE 11

A stainless steel wire guide was coated with stabilizing polymer with the following solution and dried ten minutes at 70°C.

nitrocellulose	64.6 gm
dibutylphthalate	24.3 gm
camphor	17.9 gm
polyvinylbutyral	22.5 gm

(continued)

acetone	28.4 ml
ethanol	306.1 ml
butylacetate	257.0 ml
ethylacetate	499.2 ml
toluene	552.8 ml
isopropanol	27.5 ml
dimethylformamide	200.0 ml

The sample was then overcoated with hydrophilic polymer with the following solution and dried ten (10) minutes at 70°C.

PVP	1.0 gm
ethanol	9.0 ml
dimethylformamide	2.0 ml

This coating was insoluble in water and was very lubricious.

EXAMPLE 12

The coating method of example 11 was repeated on an acrylic surface and also produced a coating that was insoluble in water and very lubricious.

EXAMPLE 13

Nylon tubing was coated with a stabilizing and adherent polymer with the following solution and dried for five (5) minutes at 65°C.

nitrocellulose	32.3 gm
polyurethane	11.2 gm
dibutylphthalate	12.2 gm
camphor	9.0 gm
polyvinylbutyral	11.2 gm
acetone	25 ml
ethanol	254 ml
butylacetate	225.3 ml
ethylacetate	439.2 ml
toluene	467.8 ml
isopropanol	13.8 ml
dimethylformamide	100 ml

The sample was then coated with hydrophilic polymer with the following solution and dried five (5) minutes at 65°C.

PVP	1.0 gm
nitrocellulose	0.12 gm
ethanol	9.0 ml
dimethylformamide	3.0 ml
ethylacetate	0.4 ml

This coating was insoluble in water and was very lubricious.

EXAMPLE 14

Polyurethane tubing was coated with the following stabilizing polymer solution and dried five (5) minutes at 65°C.

nitrocellulose	64.6 gm
dibutylphthalate	24.3 gm
camphor	17.9 gm
polyvinylbutyral	22.5 gm
acetone	28.4 ml
ethanol	306.1 ml
butylacetate	257.0 ml
ethylacetate	449.2 ml
toluene	552.8 ml
isopropanol	27.5 ml
dimethylformamide	200.0 ml

This sample was then overcoated with the following hydrophilic polymer solution and dried five minutes at 65°C.

PVP	1.0 gm
ethanol	9.0 ml
dimethylformamide	2.0 ml

This sample coating was insoluble in water and very lubricious when wet.

EXAMPLE 15

Polyvinylchloride tubing was treated in the same way as the nylon tubing in example 13. The resulting coating was insoluble and very lubricious.

EXAMPLE 16

A sample of styrene-butadiene tubing was coated with stabilizing and adherent polymer with the following solution and dried five (5) minutes at 80°C.

nitrocellulose	32.3 gm
polyurethane	10.0 gm
dibutylphthalate	12.2 gm
camphor	9.0 gm
polyvinylbutyral	11.2 gm
acetone	25 ml
ethanol	264 ml
butylacetate	226.3 ml
ethyl acetate	439.2 ml
toluene	467.8 ml
isopropanol	13.8 ml
dimethyformamide	100 ml

The sample was then coated with the following hydrophilic polymer solution and dried five minutes at 80°C.

PVP	1.0 gm
ethanol	9.0 ml
dimethylformamide	3.0 ml
water	0.5 ml

This sample was insoluble in water and was lubricious when wet.

EXAMPLE 17

This example shows how solvent(s) can be added which improves adhesion by etching or interacting with the layer onto which it is being coated. Several samples of polyurethane tubing were coated with the following stabilizing polymer solution.

nitrocellulose	64.6 gm
dibutylphthalate	24.3 gm
camphor	17.9 gm
polyvinylbutyral	22.5 gm
acetone	28.4 ml
ethanol	306.1 ml
butylacetate	257.0 ml
ethyl acetate	499.2 ml
toluene	552.8 ml
isopropanol	27.5 ml

(continued)

dimethylformamide	200.0 ml

Samples coated as above were then coated with one of the following solutions containing various amounts of dimethylformamide or acetic acid, which interact with the surface being coated in order to promote adhesion:

(a) Coat with the following hydrophilic polymer solution and dry five (5) minutes at 70°C.

PVP	1.0 gm
ethanol	9.0 ml
dimethylformamide	3.0 ml

This hydrophilic coating adhered well, was insoluble in water, and was very lubricious.

(b) Coat with hydrophilic polymer, 10% (w/v) PVP in ethanol and dry five (5) minutes at 70°C. This hydrophilic coating dissolved in water and came off.

(c) Coat with the following hydrophilic polymer solution and dry five (5) minutes at 70°C.

PVP	1.0 gm
ethanol	9.0 ml
dimethylformamide	1.0 ml

This sample resisted removal when wet, but was not as resistant to wet abrasion as the sample above containing three (3) ml of dimethylformamide.

(d) Coat with the following hydrophilic polymer solution and dry five (5) minutes at 70°C.

PVP	1.0 gm
ethanol	9.0 ml
acetic acid	3.0 ml

This hydrophilic coating adhered well, was insoluble in water, and was very lubricious.

EXAMPLE 18

In this example, the hydrophilic polymer and the stabilizing polymer were combined into a single solution, which was coated on polyurethane tubing and dried five (5) minutes at 80°C:

PVP	0.5 gm
nitrocellulose	0.056 gm
methylethylketone	13.7 ml
isopropanol	0.024 gm

(continued)

acetic acid	1.0 ml

This produced a single-layer coating that was lubricious when wet and was resistant to wet abrasion.

EXAMPLE 19

The following solution is coated on polyurethane tubing and dried (5) minutes at 80°C.

PVP	1.5 gm
Polyethylene Glycol	2.7 gm
Ethanol	68.8 gm
Isopropanol	18.0 gm
4-Butyrolactone	8.0 gm

In this example, the hydrophilic polymer was combined in a solution which contains at least one solvent which swells the substrate onto which the coating is applied. By swelling the substrate, some of the hydrophilic polymer molecules become entrained in the surface of the substrate after the solvents are evaporated.

Because some of the hydrophilic polymer is tightly bound into the substrate surface, it is made resistant to wet abrasion and produces a single-layer coating that is lubricious when wet.

EXAMPLES 20-24

The following solutions are prepared, dip-coated onto an 8 french polyurethane tube, and thereafter dried for 10 minutes at 80°C.

INGREDIENT	Ex. 20	Ex. 21	Ex. 22	Ex. 23	Ex. 24
10% PV Pin	4.0 g	4.0 g	4.0 g	4.0 g	4.0 g
Benzyl Alcohol	---	24.4 g	16.0 g	16.0 g	16.0 g
N,N, Dimethyl Acetamide	---	---	7.5 g	---	---
Glacial Acetic Acid	---	---	---	7.5 g	---
N-Methyl-2-Pyrrolidone	---	---	---	---	7.5 g
Denatured Ethanol	25.3 g	---	1.8 g	1.8 g	1.8 g

To evaluate the performance of coated lubricious layers with regard to wet lubricity and wet abrasion resistance the following test method was used. After the coating was dried to remove the organic solvents, a solution of Gentian Violet (such as Cat. No. 3240 from Ricca Chemical Company) is applied to the coated surface using a brush or cotton swab. This dye is strongly absorbed into the lubricious layer, but not into the plastic substrate. Next, the dyed sample is held under cold gently running water. After rinsing the samples with water, they are rubbed briskly between the thumb and forefinger of one hand using a firm grip. In cases where adhesion to the plastic substrate is very poor, the coated layer may wash off completely from the surface as evidenced by washing off of substantially all of the dye. In cases where the coated layer has penetrated too far into and/or become to hardened as by incorporation of too much polymeric or cross-linking agent into the coating, the dye stain can be very strong after rinsing. During the finger rubbing test, most or all of such coated layers will stay on the plastic substrate, as evidenced by retention of most of the dye, but they will not feel very lubricious. Intermediate between these extremes are coatings that have a more desirable balance of lubricious feel and resistance to removal by wet rubbing. An ability to make such qualitative assessments is quickly devel-

oped by persons skilled in evaluating physical properties of various plastic or other materials.

The coating of Example 20 washed off completely when held under cold running water, indicating that there was little or no penetration into the polyurethane and hardening of the coating. This is expected since ethanol shows very low solvent activity toward this polyurethane surface.

The outermost portion of the coatings of Examples 21 and 23 rubbed off when wet, but a thin layer remained that was very lubricious. The retained dye intensity was intermediate. These samples were judged to have very good balance between resistance to wet abrasion and lubricity.

The coatings of Examples 22 and 24 were not very lubricious when wet rubbed and the coating did not feel swollen by water in comparison to Examples 21 and 23. Samples were extremely resistant to rubbing off when wet as evidenced by a much more intense residual dye stain after wet rubbing when compared to Examples 21 and 23. These are examples where the solvent is too active so that little lubricity results.

These samples show how the performance of the lubricious layer can be adjusted to balance the resistance to wet rub off and the lubricity by selecting and using solvents alone or in combination that provide a sufficient degree of activity.

EXAMPLE 25

A solution was made as follows:

Polyvinylpyrrolidone	0.4 g
Denatured Ethanol	19.6 g
Benzyl Alcohol	10.0 g

This solution was dip coated on polyurethane tubing and then drying for 22 minutes at 80°C. A solution of Gentian Violet is applied to the coated surface as detailed in Examples 20-24. When tested, this coating was fairly resistant to wet ruff-off and was very lubricious. Comparing it to the coating of Example 21, it was a little more lubricious, but it was somewhat less resistant to wet rub-off.

EXAMPLE 26

The following solution was dip coated over polyurethane tubing and dried 12 minutes at 80°C. A solution of Gentian Violet is applied to the coated surface as detailed in Examples 20-24.

Polyvinylpyrrolidone	0.4 g
Benzyl Alcohol	10.5 g
Denatured Ethanol	3.6 g
N,N, Dimethylacetamide	5.0 g

This coating was very lubricious and a lubricious layer remained on the surface after vigorous wet rubbing which would not be removed.

EXAMPLE 27

The following solution was dip coated on polyvinyl chloride tubing and dried 12 minutes at 80°C.

Polyvinyl Pyrrolidone	0.9 gm
Methyline Chloride	5.0 gm

(continued)

N-Methyl-2-Pyrrolidone	10.0 gm

A solution of Gentian Violet is applied to the coated surface as detailed in Examples 20-24. After cooling, the coating was tested for wet lubricity and wet rub resistance by using the aforementioned Gentian Violet test regimen.

This coating was very lubricious and a lubricious layer remained on the surface after vigorous wet rubbing which could not be removed.

The examples provided above are not meant to be exclusive. Many other variations of the present invention, including the use of other cosolvents and polymer mixtures, would be obvious to those skilled in the art, and are contemplated to be within the scope of the appended claims.

Claims

1. A composition comprising:

   a hydrophilic polymer selected from the group consisting of polyvinylpyrollidone, polyvinylpyrollidone-polyvinyl acetate copolymer, a mixture thereof with the proviso that the hydrophilic polymer does not contain a silane compound;
   a water-insoluble stabilizing polymer selected from the group consisting of a cellulose ester, a copolymer of polymethyl vinyl ether and maleic anhydride, an ester of the copolymer, and nylon and a mixture thereof;
   said composition being substantially more slippery when wet than when dry, resistant to removal by wet abrasion, and preferably wherein the composition is essentially insoluble in aqueous solution.

2. A lubricious composite coating wherein the composite coating comprises: an outer layer having an exposed outer surface, said outer layer comprising a hydrophilic polymer selected from the group consisting of polyvinylpyrollidone, polyvinylpyrollidone-polyvinyl acetate copolymer, a mixture of the above, and the like with the provisio that the hydrophilic polymer does not contain a silane compound, an inner layer comprising a water-insoluble stabilizing polymer selected from the group consisting of a cellulose ester, a copolymer of polymethyl vinyl ether and maleic anhydride, an ester of the copolymer, and nylon and a mixture of the foregoing; said composite being substantially more slippery when wet than when dry, resistant to removal by wet abrasion, and essentially insoluble in aqueous solution, the ratio of said hydrophilic polymer to said stabilizing polymer altering the degree of wet lubricity, resistance to removal, and insolubility of said composite.

3. The composite coating of claim 2, wherein the stabilizing polymer includes a hydrophilic polymer.

4. The composite coating of claim 2 or claim 3, wherein said outer layer includes a stabilizing polymer.

5. The composite coating according to any one of claims 2 to 4 wherein said hydrophilic polymer is selected from the group consisting of polyvinylpyrollidone and polyvinylpyrollidone-polyvinyl acetate.

6. The composite coating according to any one of claims 1 to 5 wherein the stabilizing polymer is selected from the group consisting of cellulose acetate, cellulose acetate butyrate, cellulose acetate proprionate, cellulose nitrate, ethyl cellulose, and hydroxyethyl cellulose.

7. The composite coating according to any one of claims 2 to 6 wherein the coating includes a plasticizing agent.

8. The composite coating of claim 7, wherein the plasticizing agent is selected from the group consisting of camphor, polyvinyl butyral, dibutylphthalate, castor oil, dioctyl phthalate, acetyl tributyl citrate, dibutyl sebacate, sebacic acid and alkyl resin.

9. The composite coating according to any one of claims 2 to 8 wherein the coating includes an adherent polymer.

10. The composite coating of claim 9, wherein the adherent polymer is selected from the group consisting of polyester, polyurethane, styrene polybutadiene, acrylic resin, polyvinylidene chloride, polycarbonate, and polyvinylchloride.

11. An article having thereon a lubricious composite coating according to any one of claims 2 to 10 wherein the inner layer of the composite coating is adhered to the article.

12. The article according to claim 11, wherein the substrate is a metallic substrate, a glass substrate, or a polymeric substrate selected from the group consisting of polyurethane, polyvinylchloride, polyacrylate, polycarbonate, polystyrene, polyester resins, polybutadiene-styrene copolymers, nylon, polypropylene, polybutylene, teflon, silicon and polyvinyl acetal.

13. A lubricious hydrophilic coating for a polymer surface which is substantially more slippery when wet than when dry, is essentially insoluble in aqueous solution, and is resistant to removal by wet abrasion comprising the composition of claim 1 but wherein the coating comprises a single layer of a hydrophilic polymer selected from the group consisting of polyvinylpyrrolidone, polyvinylpyrrolidone polyvinyl acetate copolymer, and a mixture thereof, and a water-insoluble stabilizing polymer selected from the group consisting of a cellulose ester, nylon, and a mixture thereof.

14. The coating of claim 13 which is suitable for application to a polymer surface comprising a polymer selected from the group consisting of polyurethane, polyvinylchloride, polyacrylate, polycarbonate, polystyrene, polyester resins, polybutadiene-styrene copolymers, nylon, polypropylene, polybutylene, teflon, silicon, and polyvinyl acetal.

15. The coating of claim 13 or claim 14, wherein said hydrophilic polymer is selected from the group consisting of polyvinylpyrrolidone and polyvinylpyrrolidone-vinyl acetate, said stabilizing polymer is nitrocellulose, and said organic polymeric surface is polyurethane.

16. A lubricious hydrophilic coating for a polymer surface which is substantially more slippery when wet than when dry, is essentially insoluble in aqueous solution, and is resistant to removal by wet abrasion comprising a composition according to claim 1 but wherein the coating comprises a single layer of a hydrophilic polymer selected from the group consisting of polyvinylpyrrolidone, polyvinylpyrrolidone polyvinyl acetate copolymer, and a mixture thereof, and a water-insoluble stabilizing polymer selected from the group consisting of a cellulose ester, cellulose acetate butyrate, cellulose acetate propionate, cellulose nitrate, ethyl cellulose and hydroxyethylcellulose, said hydrophilic polymer coating having an exposed outer surface and an interfacing surface with said polymer surface, said hydrophilic coating having a high degree of cross-linking or inter-molecular mingling between said hydrophilic polymer and said polymer surface at said interfacing surface relative to said outer surface.

17. The coating of claim 16, which is suitable for application to a polymer surface comprising a polymer selected from the group consisting of polyurethane, polyvinylchloride, polyacrylate, polycarbonate, polystyrene, polyester resins, polybutadiene-styrene copolymers, nylon, polypropylene, polybutylene, teflon, silicon, and polyvinyl acetal.

18. The coating of claim 17, wherein the degree of lubricity and resistance to wet abrasion is controlled in part by the degree of cross-linking or intermolecular mingling between said hydrophilic polymer and said polymer surface.

19. A lubricious hydrophilic coating for a polymer surface comprising the compostion according to claim 1, the coating comprising a single layer of: a hydrophilic polymer having an exposed outer surface and an interfacing surface and being selected from the group consisting of polyvinylpyrrolidone, polyvinylpyrrolidone polyvinyl acetate copolymer, and a mixture thereof; a water-insoluble stabilizing polymer selected from the group consisting of a cellulose ester, cellulose acetate butyrate, cellulose acetate propionate, cellulose nitrate, ethyl cellulose, and hydroxyethylcellulose; and a cosolvent for both said hydrophilic polymer and said polymer surface, said hydrophilic polymer having a high degree of cross-linking or intermolecular mingling with said polymer surface interfacing said polymer surface relative to said outer surface; said coating being substantially more slippery when wet than when dry and resistant to removal by wet abrasion.

20. A lubricious hydrophilic coating comprising a composition according to claim 1, the coating comprising a single layer of: a lubricious hydrophilic polymer comprising polyvinylpyrrolidone, capable of penetrating a polymer surface of a substrate comprising polyurethane or polyvinyl chloride via use of a cosolvent for both polyvinylpyrrolidone and polyurethane or polyvinyl chloride, said hydrophilic polymer having an exposed outer surface and an interfacing surface with said polymer surface, said hydrophilic coating having a high degree of cross-linking or intermolecular mingling between the polyvinylpyrrolidone and polyurethane or polyvinyl chloride at said interfacing surface relative to said outer surface; and a water-insoluble stabilizing polymer selected from the group consisting of a cellulose ester, cellulose acetate butyrate, cellulose acetate propionate, cellulose nitrate, ethyl cellulose, and hydroxyethylcellulose; said hydrophilic coating being substantially more slippery when wet than when dry, is essentially insoluble in aqueous solution, and is resistant to removal by wet abrasion, the degree of lubricity and resistance to wet removal being controlled in part by the particular cosolvent used and the amount and type of stabilizing polymer

used.

21. A polymer surface having thereon a single layer of a lubricious hydrophilic coating according to any one of claims 13 to 20.

22. A polymer surface according to claim 9 wherein the polymer surface is of a polymer as defined in claim 15 or claim 17.

23. A polymer surface according to claim 21 or claim 22 wherein the polymer surface is the surface of a biomedical device.

24. An article according to claim 11 or 12 wherein the article is a biomedical device.

Patentansprüche

1. Zusammensetzung mit

einem hydrophilen Polymer, das aus der Gruppe ausgewählt ist, die aus Polyvinylpyrrolidon, Polyvinylpyrrolidon-Polyvinylaeetat-Copolymer und einem Gemisch hiervon besteht, wobei das hydrophile Polymer keine Silanverbindung enthält,

und einem wasserunlöslichen stabilisierenden Polymer, das aus der Gruppe ausgewählt ist, die aus einem Celluloseester, einem Copolymer von Polymethylvinylether und Maleinsäureanhydrid, einem Ester des Copolymers und Nylon sowie einem Gemisch hiervon besteht,
wobei diese Zusammensetzung in feuchtem Zustand wesentlich schlüpfriger als im trockenen Zustand ist, beständig gegen Entfernung durch Naßabrieb ist und vorzugsweise die Zusammensetzung in wäßriger Lösung im wesentlichen unlöslich ist.

2. Schmierbeschichtung, die eine Außenschicht mit einer freiliegenden Außenoberfläche, wobei diese Außenschicht ein hydrophiles Polymer aus der Gruppe umfaßt, die aus Polyvinylpyrrolidon, Polyvinylpyrrolidon-Polyvinylacetat-Copolymer, einem Gemisch derselben und dergleichen besteht, wobei das hydrophile Polymer keine Silanverbindung enthält, und eine Innenschicht, die ein wasserunlösliches stabilisierendes Polymer aus der Gruppe umfaßt, die aus einem Celluloseester, einem Copolymer von Polymethylvinylether und Maleinsäureanhydrid, einem Ester des Copolymers und Nylon sowie einem Gemisch derselben besteht, umfaßt, wobei diese Zusammensetzung in feuchtem Zustand wesentlich schlüpfriger als in trockenem Zustand ist, beständig gegen Entfernung durch Naßabrieb ist und im wesentlichen in wäßriger Lösung unlöslich ist und wobei das Verhältnis des hydrophilen Polymers zu dem stabilisierenden Polymer den Grad der Naßschlüpfrigkeit, Entfernungsbeständigkeit und Unlöslichkeit der Zusammensetzung verändert.

3. Beschichtung nach Anspruch 2, bei der das stabilisierende Polymer ein hydrophiles Polymer einschließt.

4. Beschichtung nach Anspruch 2 oder 3, bei der die Außenschicht ein stabilisierendes Polymer einschließt.

5. Beschichtung nach einem der Ansprüche 2 bis 4, bei der das hydrophile Polymer aus der Gruppe Polyvinylpyrrolidon und Polyvinylpyrrolidon-Polyvinylacetat ausgewählt ist.

6. Beschichtung nach einem der Ansprüche 1 bis 5, bei der das stabilisierende Polymer aus der Gruppe Celluloseacetat, Celluloseacetatbutyrat, Celluloseacetatpropionat, Cellulosenitrat, Ethylcellulose und Hydroxyethylcellulose ausgewählt ist.

7. Beschichtung nach einem der Ansprüche 2 bis 6, bei der die Beschichtung ein Weichmachermittel einschließt.

8. Beschichtung nach Anspruch 7, bei der das Weichmachermittel aus der Gruppe Kampfer, Polyvinylbutyral, Dibutylphthalat, Rizinusöl, Dioctylphthalat, Acetyltributylcitrat, Dibutylsebacat, Sebacinsäure und Alkylharz ausgewählt ist.

9. Beschichtung nach einem der Ansprüche 2 bis 8, bei der die Beschichtung ein Haftungspolymer einschließt.

10. Beschichtung nach Anspruch 9, bei der das Haftungspolymer aus der Gruppe Polyester, Polyurethan, Styrolpolybutadien, Acrylharz, Polyvinylidenchlorid, Polycarbonat und Polyvinylchlorid ausgewählt ist.

11. Gegenstand mit einer Schmierbeschichtung nach einem der Ansprüche 2 bis 10 darauf, in welcher die Innenschicht der Beschichtung an dem Gegenstand anhaftet.

12. Gegenstand nach Anspruch 11, bei dem das Substrat ein metallisches Substrat, ein Glassubstrat oder ein Polymersubstrat aus der Gruppe Polyurethan, Polyvinylchlorid, Polyacrylat, Polycarbonat, Polystyrol, Polyesterharze, Polybutadien-Styrol-Copolymer, Nylon, Polypropylen, Polybutylen, Teflon, Silicon und Polyvinylacetal ist.

13. Hydrophile Schmierbeschichtung für eine Polymeroberfläche, die in nassem Zustand wesentlich schlüpfriger als in trockenem Zustand ist, in wäßriger Lösung im wesentlichen unlöslich ist und beständig gegen Entfernung durch Naßabrieb ist, mit der Zusammensetzung nach Anspruch 1, worin aber die Beschichtung eine einzelne Schicht eines hydrophilen Polymers aus der Gruppe Polyvinylpyrrolidon, Polyvinylpyrrolidon-Polyvinylacetat-Copolymer sowie eines Gemisches hiervon ausgewählt ist und ein wasserunlösliches stabilisierendes Polymer aus der Gruppe, die aus einem Celluloseester, Nylon und einem Gemisch hiervon besteht, umfaßt.

14. Beschichtung nach Anspruch 13, welche für die Aufbringung auf einer Polymeroberfläche geeignet ist, die ein Polymer aus der Gruppe Polyurethan, Polyvinylchlorid, Polyacrylat, Polycarbonat, Polystyrol, Polyesterharze, Polybutadien-Styrol-Copolymere, Nylon, Polypropylen, Polybutylen, Teflon, Silicon und Polyvinylacetal umfaßt.

15. Beschichtung nach Anspruch 13 oder 14, bei der das hydrophile Polymer aus der Gruppe Polyvinylpyrrolidon und Polyvinylpyrrolidon-Vinylacetat ausgewählt ist, wobei das stabilisierende Polymer Nitrocellulose und die organische Polymeroberfläche Polyurethan sind.

16. Hydrophile Schmierbeschichtung für eine Polymeroberfläche, die in feuchtem Zustand wesentlich schlüpfriger als in trockenem Zustand ist, in wäßriger Lösung im wesentlichen unlöslich ist und beständig gegen Entfernung durch Naßabrieb ist, mit einer Zusammensetzung nach Anspruch 1, worin aber die Beschichtung eine einzelne Schicht eines hydrophilen Polymers aus der Gruppe Polyvinylpyrrolidon, Polyvinylpyrrolidon-Polyvinylacetat-Copolymer und eines Gemisches hiervon und ein wasserunlösliches stabilisierendes Polymer aus der Gruppe eines Celluloseesters, Celluloseacetatbutyrat, Celluloseacetatpropionat, Cellulosenitrat, Ethylcellulose und Hydroxyethylcellulose umfaßt, wobei diese hydrophile Polymerbeschichtung eine freiliegende Außenoberfläche und eine Grenzfläche mit der Polymeroberfläche hat und wobei die hydrophile Beschichtung einen hohen Vernetzungsgrad oder intermolekularen Vermischungsgrad zwischen dem hydrophilen Polymer und der Polymeroberfläche an der Grenzfläche in bezug auf die Außenfläche hat.

17. Beschichtung nach Anspruch 16, welche für eine Aufbringung auf einer Polymeroberfläche geeignet ist, die ein Polymer aus der Gruppe Polyurethan, Polyvinylchlorid, Polyacrylat, Polycarbonat, Polystyrol, Polyesterharze, Polybutadien-Styrol-Copolymere, Nylon, Polypropylen, Polybutylen, Teflon, Silicon und Polyvinylacetal umfaßt.

18. Beschichtung nach Anspruch 17, bei der der Schmierfähigkeitsgrad und die Beständigkeit gegen Naßabrieb teilweise durch den Vernetzungsgrad oder intermolekularen Vermischungsgrad zwischen dem hydrophilen Polymer und der Polymeroberfläche gesteuert werden.

19. Hydrophile Schmierbeschichtung für eine Polymeroberfläche mit der Zusammensetzung nach Anspruch 1, wobei die Beschichtung eine einzelne Schicht eines hydrophilen Polymers mit einer freiliegenden Außenoberfläche und einer Grenzfläche, das aus der Gruppe Polyvinylpyrrolidon, Polyvinylpyrrolidon-Polyvinylacetat-Copolymer und eines Gemisches hiervon ausgewählt ist, ein wasserunlösliches stabilisierendes Polymer aus der Gruppe Celluloseester, Celluloseacetatbutyrat, Celluloseacetatpropionat, Cellulosenitrat, Ethylcellulose und Hydroxyethylcellulose sowie ein Colösungsmittel sowohl für das hydrophile Polymer als auch für die Polymeroberfläche umfaßt, wobei das hydrophile Polymer einen Vernetzungsgrad oder intermolekularen Vermischungsgrad mit der Polymeroberfläche, die die Grenzfläche zu der Polymeroberfläche bildet, in bezug auf die Außenoberfläche hat und wobei die Beschichtung in nassem Zustand wesentlich schlüpfriger als in trockenem Zustand ist und gegen Entfernung durch Naßabrieb beständig ist.

20. Hydrophile Schmierbeschichtung mit einer Zusammensetzung nach Anspruch 1, wobei die Beschichtung eine einzelne Schicht eines hydrophilen Schmierpolymers, das Polyvinylpyrrolidon umfaßt und eine Polymeroberfläche eines Substrates, das Polyurethan oder Polyvinylchlorid umfaßt, bei Verwendung eines Colösungsmittels sowohl

für Polyvinylpyrrolidon als auch für Polyurethan oder Polyvinylchlorid durchdringen kann, wobei dieses hydrophile Polymer eine freiliegende Außenoberfläche und eine Grenzfläche mit der Polymeroberfläche hat und wobei die hydrophile Beschichtung einen hohen Vernetzungsgrad oder intermolekularen Vermischungsgrad zwischen dem Polyvinylpyrrolidon und Polyurethan oder Polyvinylchlorid an der Grenzfläche in bezug auf die Außenfläche hat, und ein wasserunlösliches stabilisierendes Polymer aus der Gruppe Celluloseester, Celluloseacetatbutyrat, Celluloseacetatpropionat, Cellulosenitrat, Ethylcellulose und Hydroxyethylcellulose umfaßt, wobei die hydrophile Beschichtung in nassem Zustand wesentlich schlüpfriger als in trockenem Zustand ist, in wäßriger Lösung im wesentlichen unlöslich ist und beständig gegen Entfernung durch Naßabrieb ist und wobei der Schmierfähigkeitsgrad und die Beständigkeit gegen Naßentfernung teilweise durch das speziell verwendete Colösungsmittel und die verwendete Menge und Type des stabilisierenden Polymers gesteuert werden.

21. Polymeroberfläche mit einer einzelnen Schicht einer hydrophilen Schmierbeschichtung nach einem der Ansprüche 13 bis 20 darauf.

22. Polymeroberfläche nach Anspruch 9, bei der die Polymeroberfläche ein Polymer nach Anspruch 15 oder Anspruch 17 ist.

23. Polymeroberfläche nach Anspruch 21 oder 22, bei der die Polymeroberfläche die Oberfläche einer biomedizinischen Einrichtung ist.

24. Gegenstand nach Anspruch 11 oder 12, der eine biomedizinische Einrichtung ist.

Revendications

1. Composition comprenant :

   un polymère hydrophile choisi dans l'ensemble constitué par la polyvinylpyrrolidone, un copolymère de polyvinylpyrrolidone-acétate de polyvinyle ou un mélange de ceux-ci, avec la condition que le polymère hydrophile ne contienne pas de composé silane ;
   un polymère stabilisant insoluble dans l'eau choisi dans l'ensemble constitué par un ester de cellulose, un copolymère d'éther de polyméthyle et de vinyle et d'anhydride maléique, un ester de ce copolymère, le Nylon et un mélange de ceux-ci ;
   ladite composition étant essentiellement plus glissante à l'état humide qu'à l'état sec, résistante à l'élimination par abrasion par voie humide, et, de préférence, la composition est essentiellement insoluble en solution aqueuse.

2. Revêtement composite lubrifiant, ce revêtement composite comprenant : une couche externe ayant une surface externe exposée, ladite couche externe comprenant un polymère hydrophile choisi dans l'ensemble constitué par la polyvinylpyrrolidone, un copolymère de polyvinylpyrrolidone-acétate de polyvinyle, un mélange de ceux-ci, et analogues, avec la condition que le polymère hydrophile ne contienne pas de composé silane, une couche interne comprenant un polymère stabilisant insoluble dans l'eau choisi dans l'ensemble constitué par un ester de cellulose, un copolymère d'éther de polyméthyle et de vinyle et d'anhydride maléique, un ester de ce copolymère, le Nylon et un mélange de ceux-ci ; ledit composite étant essentiellement plus glissant à l'état humide qu'à l'état sec, résistant à l'élimination par abrasion par voie humide et essentiellement insoluble en solution aqueuse, le rapport dudit polymère hydrophile audit polymère stabilisant modifiant le degré de lubrification à l'état humide, de résistance à l'élimination et d'insolubilité dudit composite.

3. Revêtement composite selon la revendication 2, dans lequel ledit le polymère stabilisant comprend un polymère hydrophile.

4. Revêtement composite selon la revendication 2 ou la revendication 3, dans lequel ladite couche externe comprend un polymère stabilisant.

5. Revêtement composite selon l'une quelconque des revendications 2 à 4, dans lequel ledit polymère hydrophile est choisi dans l'ensemble constitué par la polyvinylpyrrolidone et un copolymère de polyvinylpyrrolidone-acétate de polyvinyle.

6. Revêtement composite selon l'une quelconque des revendications 1 à 5, dans lequel le polymère stabilisant est

choisi dans l'ensemble constitué par l'acétate de cellulose, l'acétobutyrate de cellulose, l'acétopropionate de cellulose, le nitrate de cellulose, l'éthylcellulose et l'hydroxyéthylcellulose.

7. Revêtement composite selon l'une quelconque des revendications 2 à 6, ledit revêtement comprenant un agent plastifiant.

8. Revêtement composite selon la revendication 7, dans lequel l'agent plastifiant est choisi dans l'ensemble constitué par le camphre, le polyvinylbutyral, le phtalate de dibutyle, l'huile de ricin, le phtalate de dioctyle, le citrate d'acétyltributyle, le sébacate de dibutyle, l'acide sébacique et une résine d'alkyle.

9. Revêtement composite selon l'une quelconque des revendications 2 à 8, ledit revêtement comprenant un polymère adhérent.

10. Revêtement composite selon la revendication 9, dans lequel le polymère adhérent est choisi dans l'ensemble constitué par un polyester, un polyuréthanne, le styrènepolybutadiène, une résine acrylique, le chlorure de polyvinylidène, un polycarbonate et le chlorure de polyvinyle.

11. Article dont la surface comprend un revêtement composite lubrifiant selon l'une quelconque des revendications 2 à 10, dans lequel la couche interne du revêtement composite est collée sur l'article.

12. Article selon la revendication 11, dans lequel le substrat est un substrat métallique, un substrat en verre ou un substrat polymère choisi dans l'ensemble constitué par un polyuréthanne, le chlorure de polyvinyle, un polyacrylate, un polycarbonate, le polystyrène, des résines de polyester, des copolymères de polybutadiène-styrène, le Nylon, le polypropylène, le polybutylène, le Téflon, le silicium et le polyvinylacétal.

13. Revêtement hydrophile lubrifiant pour une surface polymère, qui est essentiellement plus glissant à l'état humide qu'à l'état sec, est essentiellement insoluble en solution aqueuse et est résistant à l'élimination par abrasion par voie humide, comprenant la composition selon la revendication 1, mais ledit revêtement comprenant une couche unique d'un polymère hydrophile choisi dans l'ensemble constitué par la polyvinylpyrrolidone, un copolymère de polyvinylpyrrolidone-acétate de polyvinyle, et un mélange de ceux-ci, et un polymère stabilisant insoluble dans l'eau choisi dans l'ensemble constitué par un ester de cellulose, le Nylon et un mélange de ceux-ci.

14. Revêtement selon la revendication 13, qui est approprié à une application sur une surface polymère comprenant un polymère choisi dans l'ensemble constitué par un polyuréthanne, le chlorure de polyvinyle, un polyacrylate, un polycarbonate, le polystyrène, des résines de polyester, des copolymères de polybutadiène-styrène, le Nylon, le polypropylène, le polybutylène, le Téflon, le silicium et le polyvinylacétal.

15. Revêtement selon la revendication 13 ou la revendication 14, dans lequel ledit polymère hydrophile est choisi dans l'ensemble constitué par la polyvinylpyrrolidone et un copolymère de polyyinylpyrrolidone-acétate de vinyle, ledit polymère stabilisant est de la nitrocellulose, et ladite surface polymère organique est formée de polyuréthanne.

16. Revêtement hydrophile lubrifiant pour une surface polymère, qui est essentiellement plus glissant à l'état humide qu'à l'état sec, est essentiellement insoluble en solution aqueuse et est résistant à l'élimination par abrasion par voie humide, comprenant une composition selon la revendication 1, mais ledit revêtement comprenant une couche unique d'un polymère hydrophile choisi dans l'ensemble constitué par la polyvinylpyrrolidone, un copolymère de polyvinylpyrrolidone-acétate de polyvinyle, et un mélange de ceux-ci, et un polymère stabilisant insoluble dans l'eau choisi dans l'ensemble constitué par un ester de cellulose, l'acétobutyrate de cellulose, l'acétopropionate de cellulose, le nitrate de cellulose, l'éthylcellulose et l'hydroxyéthylcellulose, ledit revêtement polymère hydrophile ayant une surface externe exposée et une interface avec ladite surface polymère, ledit revêtement hydrophile ayant un degré élevé de réticulation ou d'emmêlement intermoléculaire entre le polymère hydrophile et ladite surface polymère à ladite interface par rapport à ladite surface externe.

17. Revêtement selon la revendication 16, qui est approprié à une application sur une surface polymère comprenant un polymère choisi dans l'ensemble constitué par un polyuréthanne, le chlorure de polyvinyle, un polyacrylate, un polycarbonate, le polystyrène, des résines de polyester, des copolymères de polybutadiène-styrène, le Nylon, le polypropylène, le polybutylène, le Téflon, le silicium et le polyyinylacétal.

18. Revêtement selon la revendication 17, dans lequel on maîtrise le degré de lubrification et de résistance à l'abrasion

par voie humide en partie au moyen du degré de réticulation ou d'emmêlement intermoléculaire entre ledit polymère hydrophile et ladite surface polymère.

19. Revêtement hydrophile lubrifiant pour une surface polymère, comprenant la composition selon la revendication 1, ledit revêtement comprenant une couche unique d'un polymère hydrophile ayant une surface externe exposée et une interface et étant choisi dans l'ensemble constitué par la polyvinylpyrrolidone, un copolymère de polyvinylpyrrolidone-acétate de polyvinyle, et un mélange de ceux-ci ; un polymère stabilisant, insoluble dans l'eau, choisi dans l'ensemble constitué par un ester de cellulose, l'acétobutyrate de cellulose, l'acétopropionate de cellulose, le nitrate de cellulose, l'éthylcellulose et l'hydroxyéthylcellulose ; et un co-solvant à la fois pour ledit polymère hydrophile et pour ladite surface polymère, ledit polymère hydrophile ayant un degré élevé de réticulation ou d'emmêlement intermoléculaire avec ladite surface polymère formant une interface avec ladite surface polymère par rapport à ladite surface externe ; ledit revêtement étant essentiellement plus glissant à l'état humide qu'à l'état sec et résistant à l'élimination par abrasion par voie humide.

20. Revêtement hydrophile lubrifiant comprenant une composition selon la revendication 1, ledit revêtement comprenant une couche unique d'un polymère hydrophile lubrifiant comprenant de la polyvinylpyrrolidone, capable de pénétrer dans une surface polymère d'un substrat comprenant un polyuréthanne ou du chlorure de polyvinyle grâce à l'utilisation d'un co-solvant à la fois pour la polyvinylpyrrolidone et le polyuréthanne ou le chlorure de polyvinyle, ledit polymère hydrophile ayant une surface externe exposée et une interface avec ladite surface polymère, ledit revêtement hydrophile ayant un degré élevé de réticulation ou d'emmêlement intermoléculaire entre la polyyinylpyrrolidone et le polyuréthanne ou le chlorure de polyvinyle à ladite interface par rapport à ladite surface externe ; et un polymère stabilisant insoluble dans l'eau choisi dans l'ensemble constitué par un ester de cellulose, l'acétobutyrate de cellulose, l'acétopropionate de cellulose, le nitrate de cellulose, l'éthylcellulose et l'hydroxyéthylcellulose ; ledit revêtement hydrophile étant essentiellement plus glissant à l'état humide qu'à l'état sec, il est essentiellement insoluble en solution aqueuse et est résistant à l'élimination par abrasion par voie humide, le degré de lubrification et de résistance à l'élimination par abrasion par voie humide étant maîtrisé en partie au moyen du co-solvant particulier utilisé et de la quantité et du type de polymère stabilisant utilisé.

21. Surface polymère revêtue d'une couche unique d'un revêtement hydrophile lubrifiant selon l'une quelconque des revendications 13 à 20.

22. Surface polymère selon la revendication 9, ladite surface polymère étant formée d'un polymère tel que défini dans la revendication 15 ou dans la revendication 17.

23. Surface polymère selon la revendication 21 ou la revendication 22, ladite surface polymère étant la surface d'un dispositif biomédical.

24. Article selon la revendication 11 ou 12, ledit article étant un dispositif biomédical.